

Production of H₂ gas from water-basalt interaction and the origin of native copper and “5-element suite” hydrothermal deposits

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Interaction of basalt and/or ultramafic rock with water at temperatures between 200 and 500°C has the potential to create large amounts (10's to 100's of mmol/L) of H₂(aq) through oxidation of ferrous silicate minerals (olivine, pyroxene) to ferric minerals such as magnetite, epidote, and/or chlorite. This H₂ may react with external fluids, promoting reduction of dissolved metals and ligands. This general idea is applied to the deposits of the Keweenaw Peninsula of Michigan, USA, where native copper forms veins and amygdules in 1.0 Ga basalt flows coeval with terrestrial, red-bed sediments. Native copper could have precipitated when an oxidized brine rich in cuprous chloride complexes mixed with basalt-sourced H₂(aq). Formation of copper-sulfide minerals was suppressed due to the sluggish rate of thermochemical sulfate reduction (TSR) at temperatures below 300°C. However, thermochemical arsenite reduction (TAR) is much faster than TSR at 150-300°C, as we have shown experimentally [1]. This helps to explain the presence of Cu-arsenide minerals, such as mohawkite (Cu₃As), in the Michigan native-copper deposits and the relative scarcity of the common Cu sulfides. A similar model may apply to the "five-element suite" (Ag-As-Co-Ni-Bi) deposit class, exemplified by the hydrothermal veins of Cobalt, Ontario. In this case, H₂(aq) derived from diabase sills is hypothesized to react with an oxidized brine rich in a polymetallic suite of elements lacking copper but rich in silver. If both arsenite and sulfate are present, arsenite will be reduced by H₂ first, based solely on kinetics. This results in precipitation of native elements (Ag, Bi), followed by Co-Ni-arsenides (safflorite, etc.), followed by sulf-arsenides (cobaltite, etc.) and lastly by common sulfides (galena, sphalerite, etc.). Although a similar model was recently proposed by others [2], we experimentally confirm the faster rate of TAR compared to TSR, and herein propose, for the first time, the importance of dissolved H₂ gas as the primary reductant driving metal precipitation.

[1] Allin & Gammons (2017) *Proc. 2017 SGA Meeting*, Quebec City, 4p.; [2] Scharrer, Kreissl & Markl (2019) *Ore Geol Rev* 113, 103025.